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SYNTHESIS OF AROMATIC POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) DIANILINES FOR USE IN HIGH-TEMPERATURE POLYIMIDES

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Abstract A series of novel aromatic Polyhedral Oligomeric Silsesquioxane (POSS) dianiline molecules has been synthesized for use in the preparation of high temperature aromatic polyimides. A general synthetic strategy was devised to improve the structure, yield, and utility of POSS dianilines over those currently available. Peripheral aromatic functionality was specifically incorporated in order to improve thermal properties and to increase compatibility with aromatic polymers. Silyloxy and/or aromatic functional groups were used to link the aniline groups to the POSS cage in order to ensure that this linkage was not a thermal weak point. Additionally, the stereochemistry of the aniline functionality has been varied to produce both meta- and para- isomers. The new dianiline monomers can be used to produce high molecular weight polyimide polymers. These dianilines have been incorporated both as pendants to the polymer backbone, and in a “bead-on-a-string” fashion by insertion into the polymer main-chain. In addition to producing POSS polyimides with superior thermal stability, these new monomers will allow full characterization and comparison of POSS-polyimides with differing structures in order to delineate the structure-property relationships of POSS and polymer architectures.

Keywords *POSS, Polyimide, Dianiline, Thermal Stability, Silsesquioxane*

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1 Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) are monodisperse oligomers of hybrid $(\text{RSiO}_{1.5})_n$ repeat units, with the octameric cage ($n = 8$) being the most common.[1-5] These molecules have found application as property enhancers in many thermosetting and thermoplastic polymer systems.[6-9] The inorganic $\text{SiO}_{1.5}$ core imparts improved thermo-oxidative stability to the polymer, while the organic functionality (alkyl or aryl) plays a major role in determining chemical compatibility with the polymer matrix.[10,11] Amine-containing POSS compounds have found application as reactants in several polymer systems.[12,13] The use of multifunctional amino POSS compounds, each possessing eight (or more) reactive sites, has been examined in epoxy, polyimide, cyanate ester, and polyurethane thermosetting resins.[14-18] For example, $(3\text{-aminopropyl})_8\text{Si}_8\text{O}_{12}$ has been examined as an additive to improve the thermo-oxidative stability of cyanate ester and epoxy resin systems.[19,20] Multifunctional aromatic silsesquioxanes have been produced from commercially available $\text{Phenyl}_8\text{Si}_8\text{O}_{12}$. The phenyl groups on each cage are first nitrated, then reduced to produce silsesquioxanes with aniline functionality in a mixture of *ortho*-, *meta*-, and *para*-locations.[14]

An alternative approach to the incorporation of multifunctional POSS anilines is to produce POSS cages that possess only two functional aniline groups. While these compounds can still be incorporated into thermosetting resins, the difunctional compounds possess well-defined structure and stereochemistry, and can be utilized to improve properties in a variety of thermoplastic polymer systems. The synthesis of a functional POSS dianiline was first achieved by the Feher group with the production of the dianiline shown in figure 1.[21] The

synthetic scheme was successful, but is not amenable to scale-up. This dianiline has been successfully used in the production of Kapton-like polyimides, which were shown to exhibit excellent resistance to the atomic oxygen flux that plagues the use of plastics in low-earth orbit applications.[22] This work demonstrated that, as the surface of the polymer is eroded, the nano-dispersed POSS cages within the polyimide matrix react with atomic oxygen to produce a thin siliceous layer that protects the underlying polymer from further oxidative erosion. Both ground-based experiments and actual flight tests on the International Space Station have demonstrated that POSS-polyimides erode at a rate at least 10 times lower than that of commercial Kapton.[23,24] However, the thermal stability of this polymer is limited by the presence of cycloaliphatic groups surrounding the POSS cage.

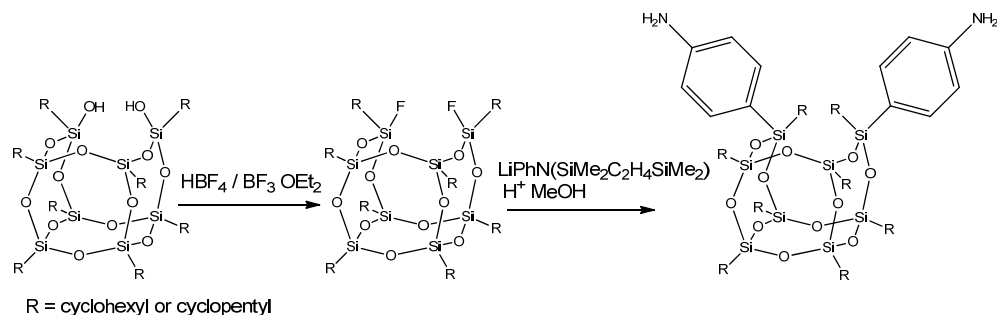


Fig. 1 The synthesis of the first POSS-dianiline, which was used to produce the first covalently bound POSS-polyimides

An alternative method used to produce a functional POSS dianiline was employed by the Wei group, which sought to improve the dielectric properties of polyimides by incorporating POSS materials.[25,26] A number of approaches to produce compounds that could be chemically linked to polyimides were attempted, with successful demonstration of the synthesis and incorporation of the

dianiline shown in figure 2.[25] The presence of cycloaliphatic groups limits the thermal stability of this polymer as well.

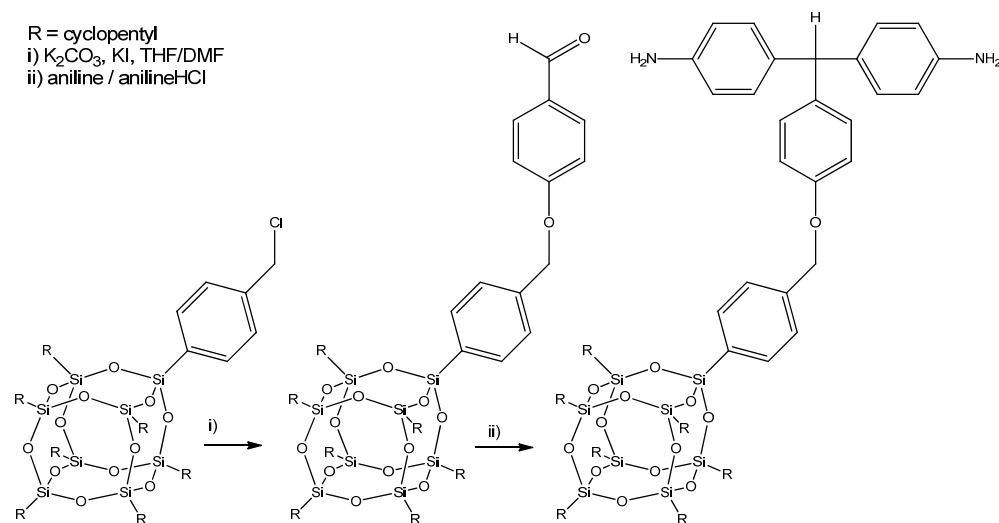


Fig. 2 The synthesis of a POSS-dianiline, used in making POSS-polyimides

A third approach by Wright et al. (figure 3) enabled a large scale synthesis from the relatively inexpensive isobutyl POSS trisilanol, which had already been “corner capped” with a reactive 3-aminopropyl group.[27] In a low-earth orbit environment, polyimides made with this POSS compound performed as well as those formed from the POSS in figure 1, with the benefit of being less expensive and more amenable to scale-up processes.[28] However, the thermal stability of this compound is limited by the presence of isobutyl peripheral groups, in addition to the thermally labile methylene linkage connecting the dianiline functionality to the POSS cage.

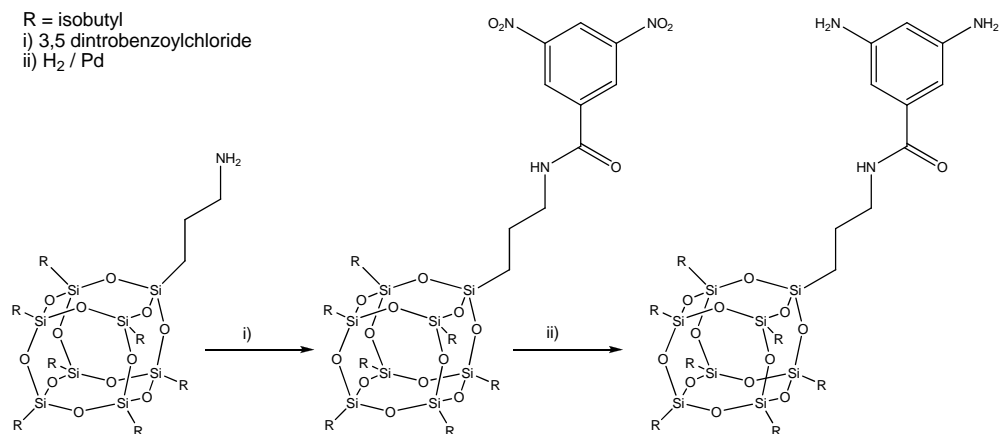


Fig. 3 Alternate synthesis of a POSS-dianiline reported by Wright et al. The thermal stability of this compound is limited by the presence of isobutyl peripheral groups, in addition to the thermally labile methylene linkages connecting the dianiline functionality to the POSS cage

Recently, Kawakami and Kakimoto have both reported using the Phenyl POSS tetrasilanol, $\text{Ph}_8\text{Si}_8\text{O}_{10}(\text{OH})_4$ (**1**), to produce a variety of new materials, including dianilines (example shown in figure 4).[29-31] The patent literature also includes a complex synthesis from the tetrasilanol to a dianiline derivative (**8a**), which was produced for this report using a different approach.[32]

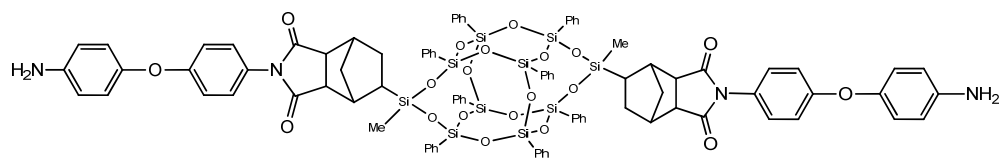


Fig. 4 A POSS-dianiline prepared by Kakimoto et al. Note that this product possesses thermally stable phenyl groups in place of the less stable aliphatic groups

While each of these compounds has been shown to improve oxidation resistance in the host polyimide polymers, interest in materials with superior thermal properties led to the development of alternative synthetic methods. Therefore, synthetic schemes were designed where products would possess

thermally stable phenyl groups and linkage to the aniline groups that were either silyloxy or aromatic in nature.[33-36] Commercially available starting materials were also desirable in terms of availability and cost. This paper describes in detail the synthesis and characterization of several new POSS-dianilines. All syntheses are amenable to scale-up.

2 Experimental

2.1 General Considerations

Phenyl-POSS tetrasilanol [$\text{Ph}_8\text{Si}_8\text{O}_{10}(\text{OH})_4$] (**1**) and phenyl-POSS trisilanol [$\text{Ph}_7\text{Si}_7\text{O}_9(\text{OH})_3$] (**2**) were obtained from Hybrid Plastics and used as received. Silicon tetrachloride (SiCl_4) and methyltrichlorosilane (CH_3SiCl_3) were obtained from United Chemical Technologies, distilled and stored under nitrogen prior to use. N-methyl-2-pyrrolidone (NMP, Tedia) was purified by distillation under reduced pressure over calcium hydride (CaH_2) and stored over 4 Å molecular sieves. Dimethylacetamide (DMAC, Aldrich) was purified by distillation under reduced pressure over barium oxide (BaO) and stored over 4 Å molecular sieves. Anhydrous diethyl ether (Burdick & Jackson), anhydrous tetrahydrofuran (THF, Aldrich), hexane (Mallinkrodt), and toluene (JT Baker) were further dried by passage thru an activated alumina column under a nitrogen atmosphere.[37] Dimethylformamide (Aldrich), methanol (Fisher), 3-[Bis(trimethylsilyl)amino]phenylmagnesium chloride solution in THF (Aldrich), 4-bromo-*N,N*-bis(trimethylsilyl)aniline (Aldrich), *p*-dioxane (Aldrich), acetic acid (Military Supply Company), and magnesium (Aldrich) were used as received.

4,4'-diaminodiphenyl ether, oxydianiline (ODA, Lancaster Synthesis) was recrystallized from DMF/toluene. Pyromellitic dianhydride (PMDA, Aldrich) was recrystallized from dioxane. Triethylamine (Aldrich) was dried by distillation from CaH_2 and stored under nitrogen prior to use. Unless otherwise noted, all manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmosphere dry box or by using standard Schlenk line techniques.[38] Dynamic vacuum distillations took place under approximately 50 millitorr pressure. NMR spectra were obtained on either a 300 or 400 MHz Bruker spectrometer. ^1H and ^{13}C NMR spectra were referenced to internal solvent; residual CHCl_3 at 7.26 ppm for proton, and CDCl_3 at 77.00 ppm for carbon. Where it was possible to make assignments, phenyl and aniline carbons were sequentially labeled as C_α , C_β , C_γ and C_δ with the carbon directly bonded to silicon identified as C_α . ^{29}Si NMR spectra were referenced to external SiMe_4 in CDCl_3 at 0 ppm, and obtained using an inverse gated 30° pulse with a 12 to 20 second delay between pulses.

2.2 Syntheses

*Ph*₇[*Si*₈*O*₁₂](*OH*) (**3**) A solution of distilled silicon tetrachloride (1.915g, 0.0113 mol) in anhydrous THF was added slowly to a stirring solution of commercially available Phenyl trisilanol (10 g, 0.0107 mol) in 50 mL anhydrous THF. This was followed by addition of NEt_3 (3.585g, 0.0354 mol) in 5 mL anhydrous THF over a period of $\frac{1}{2}$ h. The reaction mixture was stirred overnight followed by filtration. The filter cake was washed with distilled H_2O , THF, and with chloroform. The organic layer was separated and stirred with 20 mL distilled water and 2 mL 0.1 M dilute hydrochloric acid for 1 h. The organic layer was washed with H_2O ,

dilute HCl and brine solution, followed by solvent removal to form a slurry, which was precipitated into 150 mL methanol. After two hours of stirring, the mixture was filtered and the filter cake dried to give 9.19 g (92% yield) of pure Phenyl POSS-silanol. ^1H NMR (CDCl_3 , δ) 3.9 (br, 1H), 7.42 (m, 14H), 7.48 (m, 7H), 7.82 (m, 14H) ppm. ^{13}C NMR (CDCl_3 , δ) 127.88 (C_γ), 129.85, 129.97 & 129.99 (ratio = 3:3:1, C_α), 130.83 & 130.89 (ratio = 4:3, C_δ), 134.15 & 134.21 (ratio = 4:3, C_β) ppm. ^{29}Si NMR (CDCl_3 , δ) -100.39, -78.27, -78.21, -77.93 (ratio = 1:1:3:3) ppm. Elemental analysis, found (calculated): C, 51.93 (51.82); H, 3.73 (3.93).

4-[Bis(trimethylsilyl)amino]phenyl(methyl)dichlorosilane (4a) Under a nitrogen atmosphere, a solution of 4-Bromo-N, N-bis(trimethylsilyl)aniline (9.48 g, 30 mmol) in 25 mL of anhydrous THF was placed in an addition funnel and slowly added to a stirring mixture of Mg (0.912 g, 38 mmol) and anhydrous THF, already initiated with a small crystal of I_2 and a drop of 4-Bromo-N,N-bis(trimethylsilyl)aniline. The reaction was allowed to stir overnight at ambient temperature, then slowly cannulated into a 250 mL round-bottomed flask containing a stirring mixture of THF (10 mL) and trichloromethylsilane (4.485 g, 30 mmol). This was allowed to stir overnight. The solvent was removed *in vacuo* from the reaction mixture and dry hexane added to extract the product by filtration through celite. After removing all volatiles under vacuum at room temperature, the remaining yellow-colored filtrate was transferred to a 25 mL flask and distilled at 89 °C under dynamic vacuum to give the product as a colorless liquid in 87% yield (9.15 g, 26.1 mmol). ^1H NMR (CDCl_3 , δ) 0.13 (s, 18H, NSiMe_3), 1.06 (s, 3H, SiCH_3), 7.03 (m, 2H), 7.61 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , δ) 2.18

(NSiMe₃), 5.81 (SiCH₃), 127.62 (C_α), 129.95 (C_γ), 133.56 (C_β), 152.15 (C_δ) ppm.
²⁹Si NMR (CDCl₃, δ) 5.2, 18.9 (ratio = 2:1) ppm.

3-[Bis(trimethylsilyl)amino]phenyl(methyl)dichlorosilane (4b) Under a nitrogen atmosphere, a solution of 1M 3-[bis(N,N-trimethylsilyl)amino]phenyl magnesium chloride (30 mL, 30 mmol) in 25 mL of anhydrous THF was placed in an addition funnel and slowly added to a stirring mixture of trichloromethylsilane in 15 mL anhydrous THF (4.485 g, 30 mmol) and stirred overnight. The solvent was then removed *in vacuo* from the reaction mixture and dry hexane was added to extract the product by filtration through celite. After removing all volatiles under a dynamic vacuum from the filtrate, the product was distilled at 76 °C as a colorless liquid in 85% yield (8.93 g, 25.5 mmol). ¹H NMR (CDCl₃, δ) 0.13 (s, 18H, NSiMe₃), 1.06 (s, 3H, SiCH₃), 7.10 (d,d,d, 1H, J = 7.8, 2.3, 1.1 Hz), 7.29 (m, 1H), 7.35 (t, 1H, J = 7.5 Hz), 7.46 (dt, 1H, J = 7.3 Hz, 1.2 Hz) ppm. ¹³C NMR (CDCl₃, δ) 2.27 (NSiMe₃), 5.71 (SiCH₃), 128.16, 128.80, 133.62, 133.82, 134.74, 148.43 ppm. ²⁹Si NMR (CDCl₃, δ) 5.2, 18.4 (ratio = 2:1) ppm.

Di{4-[Bis(trimethylsilyl)amino]phenyl}(methyl)chlorosilane (5a) A solution of N,N-bis(trimethylsilyl)-4-bromoaniline (9.48 gm, 0.0300 mol) in 25 mL of anhydrous THF was placed in an addition funnel and slowly added to a stirring mixture of Mg (0.912 gm, 0.0380 mol) and anhydrous THF, which had been initiated with a crystal of I₂ and a drop of N,N-Bis(trimethylsilyl)-4-bromoaniline. The reaction was allowed to stir for about 2 h at ambient temperature, cannulated to a 250 mL round bottomed flask, followed by the slow addition of trichloromethylsilane (2.252 gm, 0.015 mol), and stirred overnight. The solvent was removed from the reaction mixture and dry hexane was added to

extract the product by filtration. The yellow filtrate was transferred to a distillation flask and all volatiles were removed under dynamic vacuum. The residual viscous liquid was distilled using a Kugelrohr apparatus to give di(N,N-bis(trimethylsilyl)aminophenylchloromethylsilane, as a colorless, viscous liquid in 90% yield. ^1H NMR (CDCl_3 , δ) 0.09 (36H, NSiMe_3), 0.92 (s, 3H, SiCH_3), 6.96 (dd, 4H), 7.48 (dd, 4H) ppm. ^{13}C NMR (CDCl_3 , δ) 1.69 (SiCH_3), 2.39 (NSiMe_3), 129.22 (C_α), 129.99 (C_γ), 134.74 (C_β), 150.87 (C_δ) ppm. ^{29}Si NMR (CDCl_3 , δ) 4.83, 10.70 (ratio = 4:1) ppm.

di{3-[Bis(trimethylsilyl)amino]phenyl}(methyl)chlorosilane (5b) Under a nitrogen atmosphere, a solution of 1M 3-[Bis(N,N-trimethylsilyl)amino]phenyl magnesium chloride (30 mL, 30 mmol) in 25 mL of anhydrous THF was placed in an addition funnel, slowly added to a stirring mixture of trichloromethylsilane in 15 mL anhydrous THF (2.252 g, 15 mmol), and stirred overnight. The solvent was removed from the reaction mixture under vacuum, and dry hexane was added to extract the product by filtration. The filtrate was transferred to a distillation flask and all volatiles were removed under dynamic vacuum. The residual viscous liquid was distilled using a Kugelrohr apparatus to give the product, as a colorless, viscous liquid in 90% yield. ^1H NMR (CDCl_3 , δ) 0.08 (s, 36H, NSiMe_3), 0.93 (s, 3H, SiCH_3), 7.00 (dt, 2H, $J = 7.5$ Hz, 1.9 Hz), 7.16 (m, 2H), 7.28 (t, 2H, $J = 7.5$ Hz), 7.32 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , δ) 1.06 (SiCH_3), 2.33 (NSiMe_3), 128.52, 129.25, 132.43, 135.10, 135.88, 147.97 ppm. ^{29}Si NMR (CDCl_3 , δ) 4.83, 9.89 (ratio = 4:1) ppm.

4-[Bis(trimethylsilyl)amino]phenyltrichlorosilane (6a) A solution of 4-Bromo-N,N-bis(trimethylsilyl)aniline (9.48 g, 30 mmol) in 25 mL of anhydrous THF was

placed in an addition funnel and slowly added to a stirring mixture of Mg (0.912 g, 38 mmol) and anhydrous THF initiated with a crystal of I₂ and a drop of 4-Bromo-N,N-bis(trimethylsilyl)aniline. The reaction was allowed to stir overnight at ambient temperature, cannulated to a 250 mL round bottom flask, and slowly added to a stirring mixture of THF (10 mL) and silicon tetrachloride (5.35 g, 31.5 mmol). This was allowed to stir overnight. The solvent was removed *in vacuo* from the reaction mixture and dry hexane was added to extract the product by filtration through celite. After removing all volatiles under a dynamic vacuum, the residual yellow colored filtrate was transferred to a 25 mL flask and distilled under dynamic vacuum to give the product, as a colorless, viscous liquid in 90% yield. ¹H NMR (CDCl₃, δ) 0.16 (s, 18H, NSiMe₃), 7.08 (m, 2H), 7.73 (m, 2H) ppm. ¹³C NMR (CDCl₃, δ) 2.50, 126.09 (C_γ), 130.34 (C_α), 134.03 (C_β), 153.89 (C_δ) ppm. ²⁹Si NMR (CDCl₃, δ) -0.74 (SiCl₃), 5.53 (SiMe₃), (ratio = 1:2) ppm.

(*p*-PhNH₂, Me)₂Ph₈[Si₁₀O₁₄] (**8a**) via protected aniline (**7a**) Under a nitrogen atmosphere, in a 50 mL round-bottom flask, phenyl POSS-tetrasilanol, Phenyl₈Si₈O₁₀(OH₄) (2.00g, 1.87 mmol) was suspended in 10 mL of anhydrous THF. To this stirred suspension, a solution of 4-[bis(N,N-trimethylsilyl)phenylaminio]methyldichlorosilane (1.376 g, 3.93 mmol) and NEt₃ (0.776 g, 7.67 mmol) in THF (10 mL) was slowly added in a drop-wise manner. After 30 minutes, the solution was filtered to remove NEt₃HCl (974 mg, 7.08 mmol, 95 % theoretical) and the solvent was removed under vacuum. Approximately 1 mL of diethyl ether was added to the product followed by 20 mL of MeOH to produce a suspension of white-colored intermediate. The trimethylsilyl groups were hydrolyzed by the addition of 1 drop of concentrated acetic acid and 1 hour of stirring. Equal-molar amounts of *cis*- and *trans*-products

were isolated by filtration and dried under a nitrogen stream to give a white powder in 77 % yield (1.922 g, 1.44 mmol). ^1H NMR (CDCl_3 , δ) 0.11 (s, 6H, CH_3), 3.3 (broad s, 4H, NH_2), 6.60 (m, 4H), 7.10 to 7.83 (m, 44H) ppm. ^{13}C NMR (CDCl_3 , δ) *cis*-product -0.31 (CH_3), 114.62 (aniline- C_γ), 124.90 (aniline- C_α), 127.33, 127.66, 127.74 (Ph- C_γ , ratio = 2:2:4), 130.06, 130.28, 130.33 (Ph- C_δ , ratio = 2:4:2), 130.75, 131.19, 132.06 (Ph- C_α , ratio = 2:2:4), 134.02, 134.11, 134.18 (Ph- C_β , ratio = 4:2:2), 134.96 (aniline- C_β), 147.52 (aniline- C_δ); *trans*-product -0.29 (CH_3), 114.76 (aniline- C_γ), 125.11 (aniline- C_α), 127.50, 127.74 (Ph- C_γ , ratio = 4:4), 130.20, 130.29, (Ph- C_δ , ratio = 4:4), 130.96, 132.05 (Ph- C_α , ratio = 4:4), 134.02, 134.14, (Ph- C_β , ratio = 4:4), 134.96 (aniline- C_β), 147.28 (aniline- C_δ) ppm. ^{29}Si NMR (CDCl_3 , δ) *cis*-product -79.4, -79.1, -78.2, -29.7 (ratio 2:2:4:2); *trans*-product -79.3, -78.2, -29.7 (ratio = 4:4:2) ppm. Elemental analysis, found (calculated): C, 55.29 (55.74); H, 4.37 (4.38); N, 1.99 (2.10).

(*m*- PhNH_2 , Me) $_2\text{Ph}_8[\text{Si}_{10}\text{O}_{14}]$ (**8b**) via protected aniline (**7b**) Under a nitrogen atmosphere, in a 50 mL round-bottom flask, phenyl POSS-tetrasilanol, $\text{Phenyl}_8\text{Si}_8\text{O}_{10}(\text{OH}_4)$ (2.00g, 1.87 mmol) was suspended in 10 mL of anhydrous THF. To this stirred suspension, a solution of 3-[bis(N,N-trimethylsilyl)phenylaminio]methyldichlorosilane (1.376 g, 3.93 mmol) and NEt_3 (0.776 g, 7.67 mmol) in THF (10 mL) was slowly added in a drop-wise manner. After 30 minutes, the solution was filtered to remove NEt_3HCl (957 mg, 6.95 mmol, 93 % theoretical) and the solvent was removed under vacuum. Approximately 1 mL of diethyl ether was added to the product followed by 20 mL of MeOH to produce a suspension of white-colored intermediate. The trimethylsilyl groups were hydrolyzed by the addition of 1 drop of concentrated acetic acid and 1 h of stirring. Equal-molar amounts of *cis* and *trans*-products

were isolated by filtration and dried under a nitrogen stream to give a white powder in 84 % yield (2.097 g, 1.57 mmol). ^1H NMR (CDCl_3 , δ) 0.58 (s, 6H, CH_3), 3.3 (broad s, 4H, NH_2), 6.74. (m, 4H), 6.99 to 7.62 (m, 44H) ppm. ^{13}C NMR (CDCl_3 , δ) -0.56 (Me); 116.68, 119.80, 123.59, 128.81, 128.82, 137.10, 145.75 & 145.77 (aniline); 127.46, 127.56, 127.65, 127.75, 130.18, 130.26, 130.33, 130.72, 130.90, 131.06, 131.88, 134.00, 134.08 & 134.11 (phenyl) ppm. ^{29}Si NMR (CDCl_3 , δ) *cis*-product -79.8, -79.4, -78.4, -30.5 (ratio = 2:2:4:2); *trans*-product -79.6, -78.4, -30.5 (ratio = 4:4:2) ppm. Elemental analysis, found (calculated): C, 55.36 (55.74); H, 4.25 (4.38); N, 2.02 (2.10).

((*p*- PhNH_2) $_2\text{Si}(\text{Me})\text{O}$) $\text{Ph}_7[\text{Si}_8\text{O}_{12}]$ (**10a**) via protected (**9a**) A solution of 0.67 g (1.2 mmol) of di(N,N-bis(trimethylsilyl)aminophenylchloromethylsilane in 2 mL dry ether was slowly added to a stirring solution of 1.08 g (1.1mmol) POSS-silanol in 5 mL dry ether and 2 mL anhydrous THF. To this was slowly added a solution of 0.116 g (1.15 mmol) of distilled triethylamine in dry ether. This was left stirring over night. The solution was filtered to remove NEt_3HCl precipitate and the solvent evaporated to a thick slurry. Compound (**9a**) was isolated by precipitation into methanol. ^{29}Si NMR (CDCl_3 , δ) -109.5, -78.3, -78.2, -78.0, -8.0, 4.5 (ratio = 1:1:3:3:1:4) ppm. It is usually more convenient to pour the slurry into 150 mL wet methanol acidified with glacial acetic acid to give POSS dianiline monomer in 98% yield. ^1H NMR (CDCl_3 , δ) 0.63 (3H, SiCH_3), 3.67 (4H, NH_2), 6.56 (4H, d J = 8.4 Hz), 7.43 (18H, m), 7.53 (7H, m), 7.84 (14H, m) ppm. ^{13}C NMR (CDCl_3 , δ) -0.38 (SiCH_3), 114.51 (aniline- C_γ), 125.55 (aniline- C_α), 127.98 & 128.06 (ratio = 3:4, Ph- C_γ), 130.32 & 130.37 (ratio = 3:4, Ph- C_α), 130.87 & 130.96 (ratio = 3:4, Ph- C_δ), 134.40 & 134.52 (ratio = 3:4, Ph- C_β), 135.62 (aniline- C_β), 147.85 (aniline- C_δ) ppm. ^{29}Si NMR (CDCl_3 , δ) -109.4, -78.3,

-78.1, -8.0 (ratio = 1:4:3:1) ppm. Elemental analysis, found (calculated): C, 54.48 (55.06); H, 4.25 (4.20); N, 2.10 (2.33).

((m-PhNH₂)₂Si(Me)O)Ph₇[Si₈O₁₂] (10b) via protected **(9b)** The same high-yield process to produce the para-derivative **10a** was followed. ¹H NMR (CDCl₃, δ) 0.68 (3H, SiCH₃), 3.32 (4H, NH₂), 6.69 (2H, d J = 6.8 Hz), 6.92 (2H, s), 7.02 (2H, d J = 7.2 Hz), 7.09 (2H, t J = 7.4 Hz), 7.42 (14H, m), 7.52 (7H, m), 7.83 (14H, m) ppm. ¹³C NMR (CDCl₃, δ) -0.65 (SiCH₃), 116.61, 120.48, 124.24, 128.85, 137.95 & 145.90 (aniline), 128.08 (Ph-C_γ), 130.29 & 130.31 (ratio = 3:4, Ph-C_α), 130.99 (Ph-C_δ), 134.39, 134.41 & 134.52 (ratio = 1:3:3, Ph-C_β) ppm. ²⁹Si NMR (CDCl₃, δ) -109.3, -78.0, -77.8, -8.2 (ratio = 1:4:3:1) ppm. Elemental analysis, found (calculated): C, 54.67 (55.06); H, 4.33 (4.20); N, 2.32 (2.33).

(p-PhNH₂)Ph₇[Si₈O₁₂] (12a) via protected **(11a)** An ethereal solution (5 mL) of phenylbis(trimethylsilyl)trichlorosilane, (0.89 g, 2.4 mmol), was added to a stirring 15 mL solution (10 mL ether and 5 mL THF) of trisilanolphenyl POSS, Ph₇Si₇O₉(OH)₃ (2.06 g, 2.2 mmol). To this mixture, an ethereal solution of triethylamine (0.697 g, 6.90 mmol) was slowly added and allowed to stir over night. The solution was filtered to remove NEt₃HCl precipitate and most of the solvent removed under vacuum to produce a slurry. The slurry was precipitated into 150 mL reagent grade methanol acidified with glacial acetic acid to give the POSS monoaniline **(12a)** in 60 % yield. ¹H NMR (CD₂Cl₂, δ) 3.90 (2H, NH₂), 6.68 (2H, d = 8 Hz), 7.40 (14H, m), 7.48 (7H, m), 7.55 (2H, d = 8 Hz), 7.78 (14H, m) ppm. ¹³C NMR (CD₂Cl₂, δ) 114.73 (aniline-C_γ), 118.07 (aniline-C_α), 128.53 (Ph-C_γ), 130.79 & 130.91 (Ph-C_α, ratio = 3:4), 131.40 & 131.43 (Ph-C_δ, ratio = 4:3), 134.59 (Ph-C_β), 136.04 (aniline-C_β), 149.83 (aniline-C_δ) ppm. ²⁹Si NMR

(CD₂Cl₂, δ) -78.50, -78.34, -76.99 (ratio = 3:4:1) ppm. Elemental analysis, found (calculated): C, 55.03 (54.98); H, 3.87 (3.94); N, 1.30 (1.34).

Copolymerization with ODA and PMDA Various proportions of POSS-dianiline monomer (**10a**) and 4,4'-oxydianiline (ODA) were reacted with pyromellitic dianhydride (PMDA) to form PMDA-(ODA/POSS-dianiline) copoly(amic acid). The copoly(amic acid) of 5 wt.% POSS/PMDA-ODA (1.9 % cage) was prepared by adding a DMAC solution (4 mL) of POSS-dianiline (**10a**) (100 mg, 0.083 mmol) into a stirring DMAC solution (4 mL) of ODA (901 mg, 4.50 mmol) under an inert atmosphere. To this solution, a DMAC suspension (4 mL) of PMDA (1000 mg, 4.585mmol) in 4mL DMAC was slowly added and allowed to stir overnight, resulting in a viscous poly(amic acid) (PAA) solution. 10 wt. % POSS (209 mg POSS, 883 mg ODA, and 1000 mg PMDA), 15 wt. % POSS (328 mg POSS, 863 mg ODA, and 1000 mg PMDA), and 20 wt. % POSS (460 mg POSS, 841 mg ODA, and 1000 mg PMDA), copoly(amic acid) solutions were obtained by using the same methodology. All copoly(amic acid) mixtures were cast on glass slides and subsequently placed in a vacuum oven at 80 °C for 4 hours, under a nitrogen purge. Imidization of POSS-PMDA-ODA was carried out by placing the samples in a nitrogen circulated vacuum oven at 120, 160, 200, 250 °C for 1 h each and then at 280 °C for 2h to ensure complete imidization.

2.3 Single crystal X-ray crystallographic analysis of *cis*- and *trans*- (8a).

Crystal data for both compounds was collected at T=173.0 (K) using Kusing Bruker 3-circle, SMARTAPEX CCD with c-axis fixed at 54.748, running on SMART V 5.625 program (Bruker AXS: Madison,2001). Graphite monochromated Mo_{K α} (λ = 0.71073 Å)

radiation was employed for data collection and corrected for Lorentz and polarization effects using SAINT V 6.22 program (Bruker AXS: Madison, 2001), and reflection scaling (SADABS program, Bruker AXS: Madison, WI, 2001). Structures were solved by direct methods (SHELXL-97, Bruker AXS: Madison, 2000) and all non-hydrogen atoms refined anisotropically using full-matrix least-squares refinement on F^2 . Hydrogen atoms were added at calculated positions when necessary.

Single crystals for *cis*-(**8a**) were grown by slow cooling in ethyl acetate, resulting in pale yellow crystals. For *cis*-(**8a**), T_r =, Triclinic, space group $P \bar{1}$, $a=13.9215(2)$ Å, $b=14.3662(2)$ Å, $c=17.57175(2)$ Å, $\alpha=96.6530(10)^\circ$, $\beta=99.1920(10)^\circ$, $\gamma=94.0300(10)^\circ$, $V=3421.09(8)$ Å³, $F(000)=1488$, $\rho_{\text{calcd}}(Z=2)=1.383$ gcm⁻³, $\mu=0.261$ mm⁻¹, approximate crystal dimensions $0.39 \times 0.35 \times 0.35$ mm³, θ range = 1.50 to 24.74° , 97201 measured data of which 15690 ($R_{\text{int}}=0.0388$, $R\sigma=0.0243$) unique with 851 refined parameters, 0 restraints were applied, final R indices [$I>2\sigma(I)$]: $R_1=0.0365$, $wR_2=0.0979$, $R_1=0.0488$, $wR_2=0.1085$ (all data), GOF on $F^2=1.036$. This data (CCDC 880830) can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif.

Clear colorless single crystals of *trans*-(**8a**) were grown by slow evaporation in tetrahydrofuran. For *trans*-(**8a**), M_r =, monoclinic, space group $P2(1)/c$, $a=10.9135(4)$ Å, $b=18.0703(7)$ Å, $c=20.7573(8)$ Å, $\alpha=90.00^\circ$, $\beta=99.7840(10)^\circ$, $\gamma=90.00^\circ$, $V=4034(3)$ Å³, $F(000)=1712$, $\rho_{\text{calcd}}(Z=2)=1.337$ gcm⁻³, $\mu=0.232$ mm⁻¹, approximate crystal dimensions $0.28 \times 0.27 \times 0.26$ mm³, θ range = 1.50 to 24.74° , 88363 measured data of which 6917 ($R_{\text{int}}=0.0693$, $R\sigma=0.0267$) unique with 619 refined parameters, 0 restraints were applied, final R indices [$I>2\sigma(I)$]: $R_1=0.0356$, $wR_2=0.0950$, $R_1=0.0448$, $wR_2=0.1010$ (all data), GOF on $F^2=1.021$. This data (CCDC 880831) can be obtained free of charge from The Cambridge Crystallographic Data Centre via

3 Results and Discussion

The goal of this work was to produce a set of high-yield, reproducible, scalable syntheses for POSS dianilines possessing maximum possible thermal stability. Two POSS starting materials were used to achieve these goals: a phenyl-POSS tetrasilanol (**1**) and a phenyl-POSS trisilanol (**2**) (See figure 5). Both of these commercially available POSS silanols react readily with appropriately substituted chlorosilanes, in the presence of triethylamine, to produce the desired products in high yield. The trisilanol (**2**) was converted to a monosilanol (**3**), which was needed to produce a POSS dianiline with an alternative architecture. A simple route to a monoaniline POSS (useful as an end-cap in polymerization) was also developed from the phenyl-POSS trisilanol.

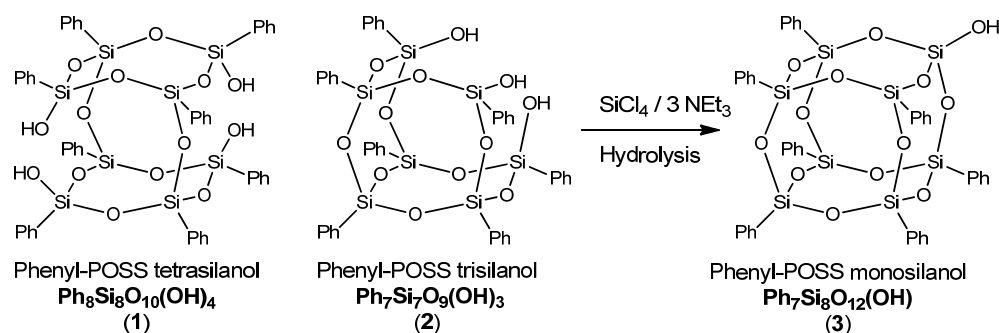


Fig. 5 Phenyl-POSS silanols used to produce POSS-anilines

As aromatic substituents impart a higher degree of thermal stability to POSS cages over their aliphatic counterparts, phenyl POSS cages were employed.[33-35] To fully maximize their thermal stability, aromatic

chlorosilanes were needed to produce the desired products and, in some cases, siloxane linkages were also used. Unlike the majority of POSS-dianilines previously reported, aliphatic linkages were avoided.

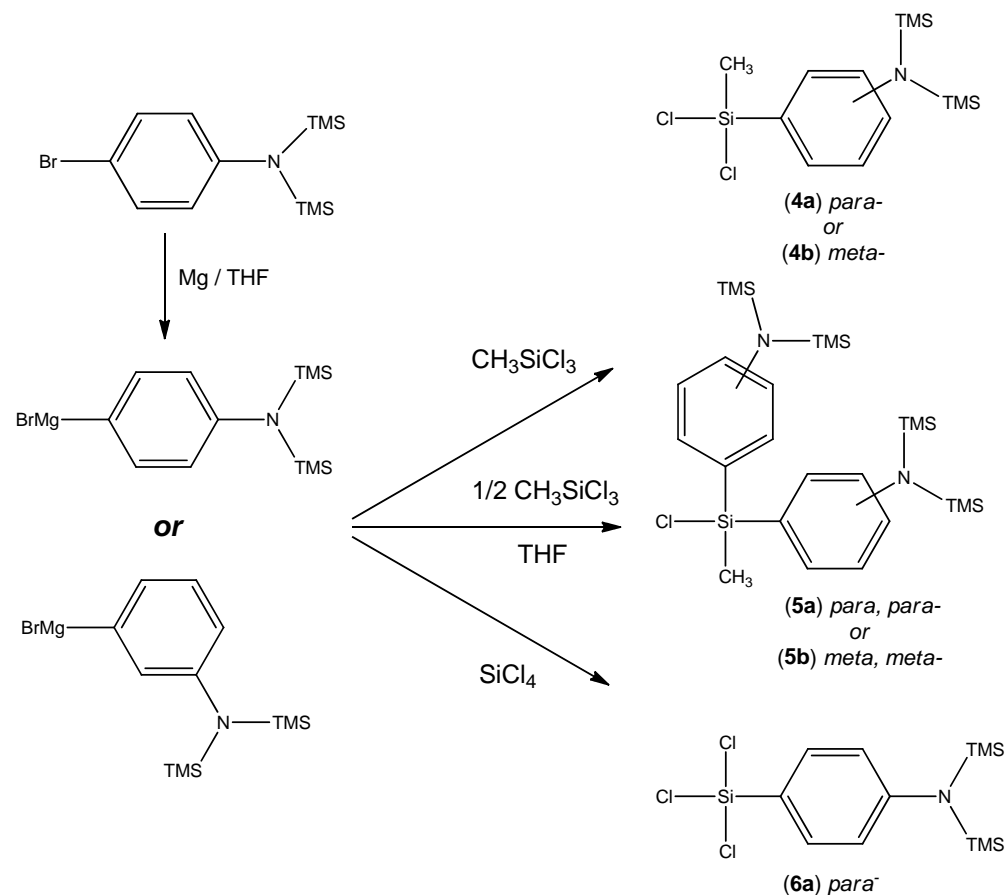


Fig. 6 Protected aniline chlorosilanes used to derivatize POSS silanols

3.1 Chlorosilane synthesis

In order to obtain the desired POSS-anilines, synthetic routes were devised to produce a series of chlorosilanes that could be reacted with various POSS silanol architectures. Chlorosilanes react readily with POSS-silanols (**1**, **2** or **3**) in the presence of triethylamine, but the nature of the reactive silicon-chloride bond requires that protected anilines be used. Outlined in figure 6 are the routes used to

make tri-, di- and mono-chlorosilanes containing TMS-protected anilines. In all cases, a Grignard reagent of a *para*- or *meta*- substituted, protected aniline was reacted with a chlorosilane. Control of the reaction is surprisingly simple. A reasonable control of stoichiometry is all that is needed to obtain a good reaction yield of the desired product. Reaction of one equivalent of Grignard reagent with a small excess of tetrachlorosilane generates a good yield of monosubstituted trichlorosilane (**6a**). It must be that the first silicon-chloride bond is much more reactive than the second silicon-chloride bond or poor yields of (**6**) would be obtained and significant amounts of $\text{Cl}_2\text{Si}(\text{Ar})_2$ and $\text{ClSi}(\text{Ar})_3$ would be generated. This is not the case. Steric crowding likely plays a major role in reducing the reactivity of silicon-chloride bonds as aromatic groups are placed about the silicon.

The same degree of control is found for reaction with methyltrichlorosilane. It is possible to add either 1 equivalent (to make **4a** and **4b**) or 2 equivalents of the protected aniline Grignard reagent (to make **5a** or **5b**) through control of stoichiometry. All chlorosilanes were isolated by distillation under dynamic vacuum and fully characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy. Their spectra are unremarkable and display the expected number of peaks in the appropriate regions. This spectroscopic data is reported in the experimental section. The ^{29}Si NMR spectrum of (**4a**) is displayed in figure 8a.

3.2 POSS dianiline synthesis

Reacting two equivalents of the dichlorosilane (**4a**) or (**4b**) with the POSS tetrasilanol (**1**) in the presence of 4 equivalents of triethylamine cleanly generates equal amounts of *cis*- and *trans*- isomers of protected POSS dianilines (**7a**) or

(7b) (see figure 7). Generally speaking it is not necessary to isolate these protected anilines. Following the reaction between the dichlorosilane (4) and the POSS tetrasilanol (1), the crude product is separated from insoluble HNEt_3Cl by filtration, and solvent removal. Addition of a small amount of diethyl ether to impart partial solubility of (7) and stirring overnight in 1 % aqueous methanol (acidified with a catalytic amount of acetic acid) cleaves the trimethylsilyl groups leaving mostly insoluble POSS dianilines (8) to be isolated by filtration. The samples were washed with methanol and dried by pulling a nitrogen stream thru the solid white powder. These materials were kept under nitrogen, because when dried under a stream of air, the dianilines slowly oxidized and became a light yellow color in appearance.

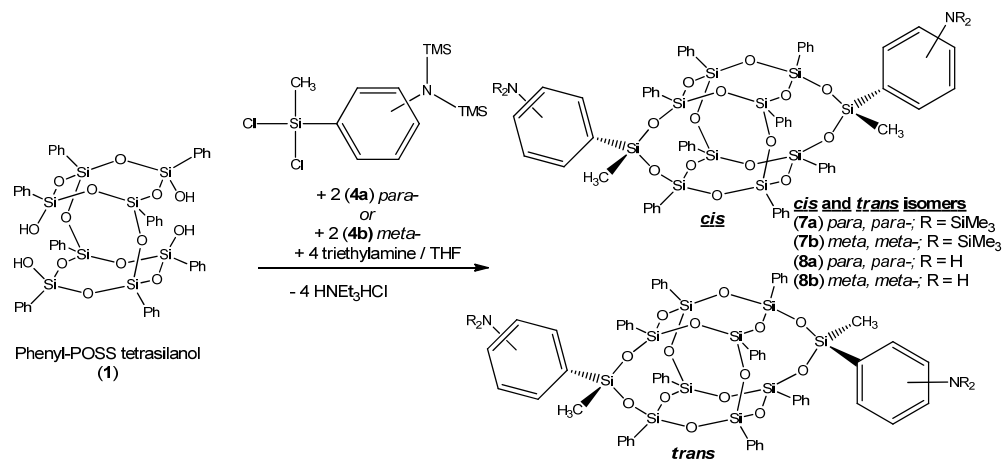


Fig. 7 Scheme illustrating the synthesis of *cis* and *trans* Phenyl-POSS dianilines derived from tetrasilanol (1)

The ^{29}Si NMR spectra (figure 8) of these compounds are interesting and somewhat complex because the synthesis generates two isomers in equal amounts. The first is a higher symmetry, lower solubility *trans*-isomer, which can be readily separated from the lower symmetry, higher solubility *cis*-isomer. Further

complicating matters is the fact that several of the ^{29}Si NMR signals are “isochronous.” Therefore, fewer signals than expected are observed.

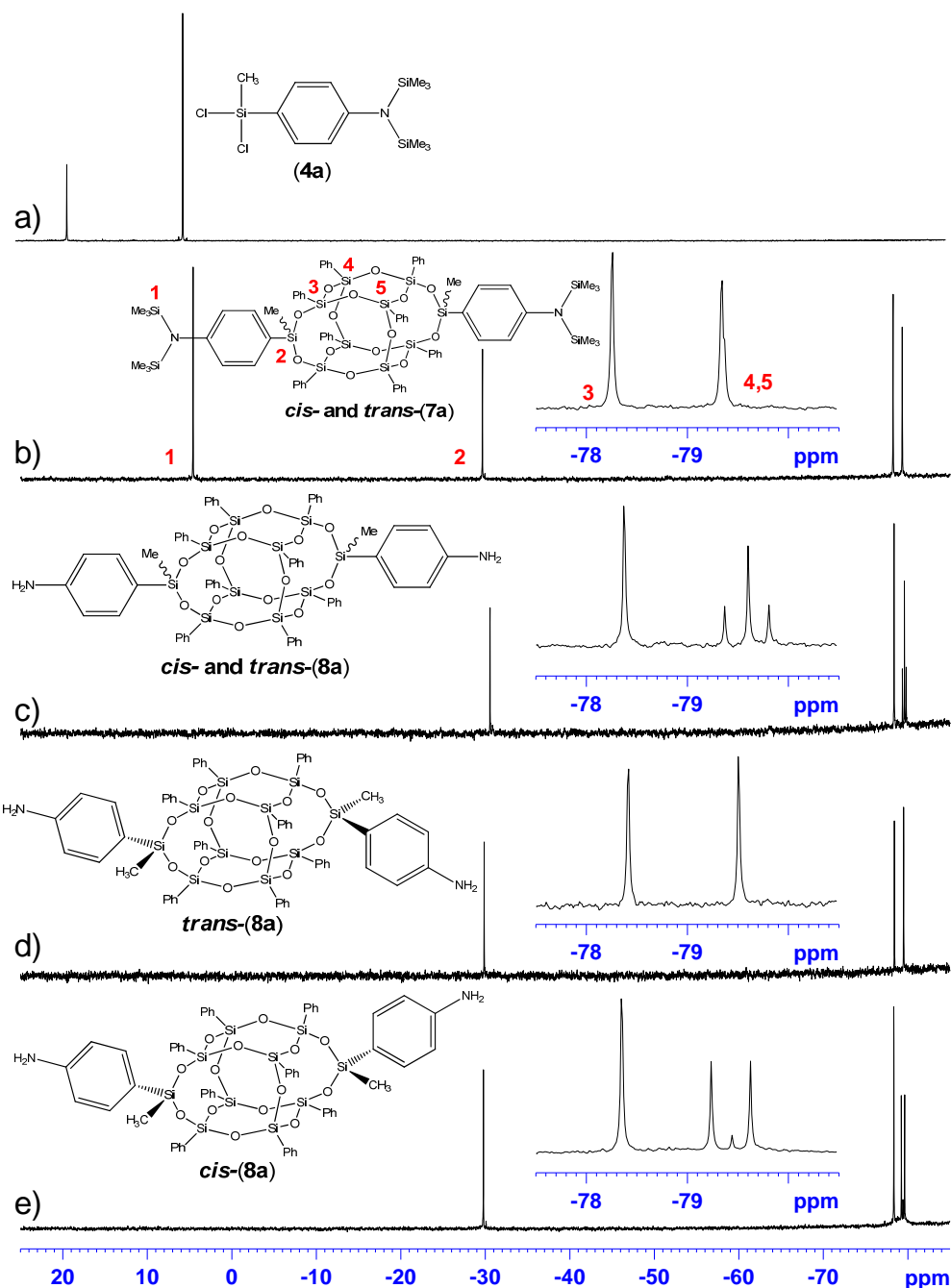


Fig. 8 ^{29}Si NMR spectra displaying regions from +25 to -85 ppm, with insets from -77.5 to -80.5 ppm. Spectra displayed for: a) dichlorosilane (4a); b) mixed *cis*- and *trans*- (7a) isomers prior to removal of the TMS protecting groups; c) mixed *cis*- and *trans*- (8a) free aniline isomers; d) pure *trans*-(8a); e) mostly *cis*-(8a)

In figure 8b, the spectrum for the *cis*- and *trans*- mixture of protected aniline (**7a**) illustrates this well. Although two geometrically different isomers are present, they are indistinguishable and a very simple spectrum is observed. There is only one peak at 8 ppm for the four trimethylsilyl groups on both isomers. There is just one peak at -30 ppm for the two silicon atoms to which the protected anilines are bound. There are two somewhat broad peaks near -78 & -79 ppm for the cage silicon atoms attached to three oxygen atoms and 1 phenyl group. Once the trimethylsilyl protecting groups are removed, the spectra become more complex (figure 8c, 8d, and 8e). The spectrum of the mixture of *cis*- and *trans*-isomers does not display the expected number resonances, but once the isomers are separated and their spectra compared, it is obvious that certain chemical shifts are isochronous. The expected three signals (-30, -78.4, and -79.5 ppm) for the higher symmetry *trans*-(**8a**) isomer and four signals (-30, -78.4, -79.3, and -79.7 ppm) for the lower symmetry *cis*-(**8a**) isomer are clearly demonstrated. This somewhat odd spectral behavior has been reported for other POSS derivatives made from tetrasilanol (**1**).[29]

Further confirmation of the absolute stereochemistry was obtained using single crystal X-ray crystallography. The structure of the *trans*-(**8a**) isomer is shown in figure 9. Monoclinic single crystals (space group P2(1)/c) were grown from THF solutions and subjected to analysis at 173 K. The R factor is less than 4 %; all bond lengths and angles are in the normal range. The structure demonstrates the near perfect symmetry that is observed in the solution state. The *trans*-aniline groups are exactly planar and related by a C2 axis of symmetry. The structure of the *cis*-(**8a**) isomer is shown in figure 10. Triclinic single crystals (space group P -1) were grown from ethyl acetate solutions and also subjected to analysis at 173 K. The R factor less than 4 %; all bond lengths and angles are in

the normal range. The structure does exhibit lower symmetry as expected from the solution state NMR spectra.

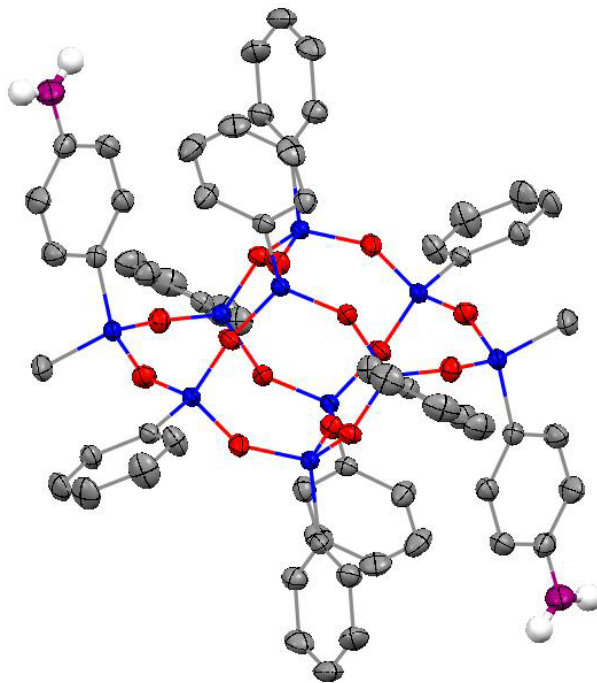


Fig. 9 Structure of *trans*-POSS dianiline (**8a**) obtained by single crystal X-ray crystallography. Gray, Carbon; Blue, Silicon; Red, Oxygen; Purple, Nitrogen; thermal ellipsoids are shown at 50%

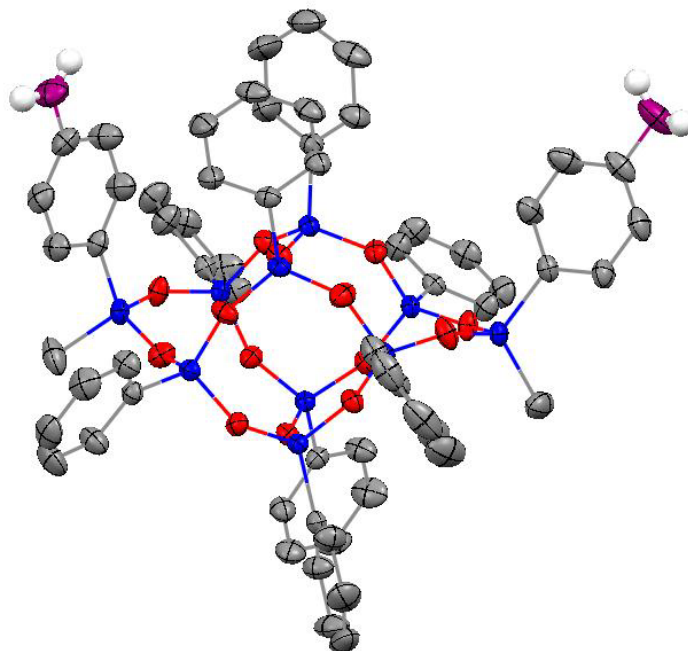


Fig. 10 Structure of *cis*-POSS dianiline (**8a**) obtained by single crystal X-ray crystallography. Gray, Carbon; Blue, Silicon; Red, Oxygen; Purple, Nitrogen; thermal ellipsoids are shown at 50%

POSS dianilines were also synthesized using a phenyl POSS trisilanol (**2**). The synthetic scheme is presented in figure 11. Trisilanol (**2**) was first capped with tetrachlorosilane to produce the $\text{Ph}_7[\text{Si}_8\text{O}_{12}]\text{Cl}$ derivative, which is easily hydrolyzed to a monosilanol (**3**). This monosilanol, isolated in over 93% yield, reacts readily with monochlorosilanes to produce the aniline derivatives (**9a**), (**9b**), (**10a**), and (**10b**) in high yield. It is not necessary to isolate the protected anilines (**9a** and **9b**). In fact, it is simpler to hydrolyze these compounds during workup to produce the desired anilines directly. As with the tetrasilanol derivatives, hydrolysis is easily achieved in wet methanol, and is catalyzed by weak acid. These white POSS anilines should be stored under nitrogen to prevent any discoloration that can occur with oxidation of the aniline group.

If a POSS monoaniline is desired for use as an end-capping agent in any condensation polymerization scheme, it can be readily produced by reacting the trisilanol (**2**) with (**6a**). This is another high-yield synthesis that produced a POSS aniline that can also be used as a telechelic head and/or tail.

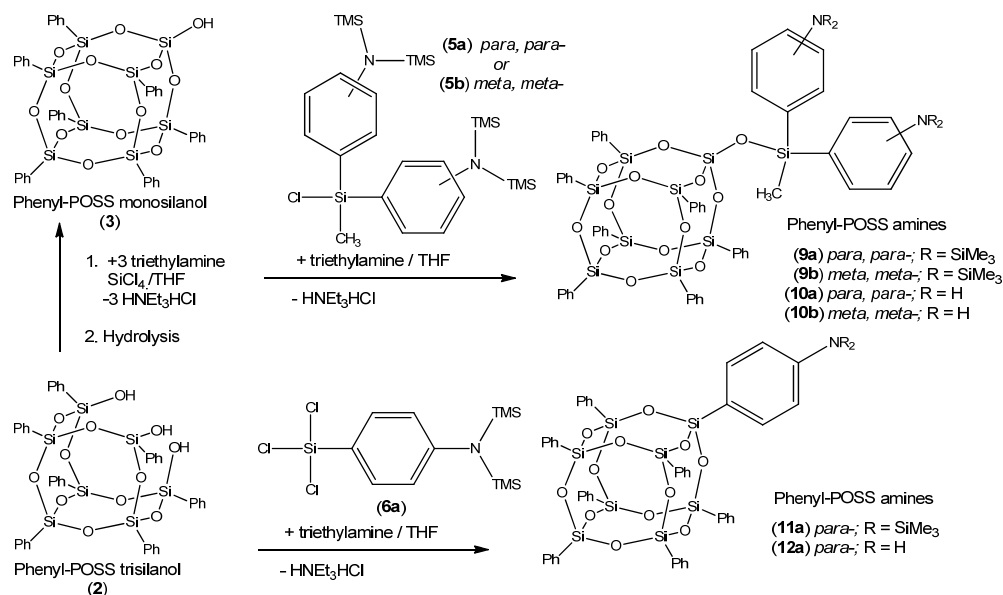


Fig. 11 Phenyl-POSS anilines derived from trisilanol (2)

3.3 POSS dianiline polymerization

All of the aforementioned POSS-dianilines can be copolymerized into polyimide systems. This work to delineate the effect of the POSS in various architectures and geometries is underway [39] and is to be the subject of a future publication. One type of polymerization is presented here in order to demonstrate the process, and confirm that the synthesis of such polyimides is possible. Summarized in figure 12 is the copolymerization of *para,para*-(10a) with oxydianiline (ODA) and pyromelitic dianhydride (PMDA).

Slow addition of a DMAC slurry of 1 molar equivalent of PMDA to a mixture of ODA and (10a) produces a viscous solution of POSS-copolymerized poly(amic acid). Solutions with 0, 10, 15, and 20 weight % (10a), respectively, were obtained. These were cast onto glass substrates and DMAC was removed by heating under a nitrogen atmosphere at 80 °C for 4 hours. Complete imidization

took place under a nitrogen atmosphere using the following temperature profile: 120 °C (1 hr), 160 °C (1 hr), 200 °C (1 hr), 250 °C (1 hr), and 280 °C (2 hr). After cooling, the films were lifted off the glass substrates with the assistance of brief water submersion. All copolymer compositions yielded films of expected toughness in relation to PMDA-ODA and did not exhibit micro-cracking in the imidized state.

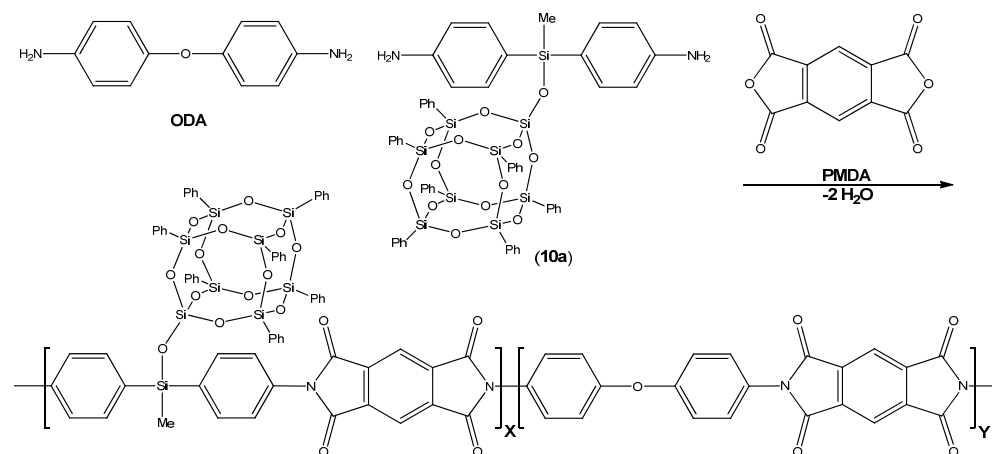


Fig. 12 Example synthesis of a POSS Kapton-like polyimide

To compare the viscoelastic properties of the copolymers to the control polyimide, non-isothermal Dynamic Mechanical Analysis (DMA) was performed on the films at a heating rate of 5 °C per minute under a nitrogen atmosphere, a strain amplitude of 15 μm , and a frequency of 1 Hz. The results are plotted in figures 13 and 14 for the (10a) and (8a) copolymers, respectively. The dependencies of storage modulus and tan delta on temperature are shown. All of the materials demonstrate absolute values of elasticity characteristic of polyimides produced from aromatic step condensation yielding weight average molecular weights in the vicinity of 50–100 KD. However, the insertion of POSS into the

backbone of the polyimide exerts different effects dependent on POSS type. For pendant-type POSS (**10a**), copolymerization has marginal impact on the glass transition temperature (T_g) as highlighted by the location of the tan delta peak, although its magnitude appears to be influenced. Film elasticity decreases with increasing POSS concentration. Contrastingly, for the bead-on-a-string POSS (**8a**), incorporation has less of an effect on elasticity but a profound influence on the location and shape of the relaxation associated with softening. The T_g is depressed by ~ 50 and ~ 60 °C for copolymers containing 16 and 32 weight percent of (**8a**), respectively. Interestingly, for the copolymer containing the highest concentration, a bimodal relaxation is witnessed suggesting the existence of two distinct phases within the material likely induced by POSS-POSS interactions.

These dissimilar observations may be explained by the nature of POSS connectivity to the polymer backbone. T_g is determined by the ability for polymer segments to participate in thermally induced cooperative translation. Translation is a function of the relative stiffness of polymer segments as well as interactions between neighboring chains. Since polyimides such as PMDA-ODA derive many of their relatively superior properties from the rigidity of their repeat units as well as charge transfer complex (CTC) interactions between the dianhydride and diamine units of neighboring chains, it is apparent that the replacement of some of the ODA units with much larger POSS monomers will reduce this type of interaction due to the sterically-hindered availability of the nitrogen donor. Offsetting this reduction in CTC interactions is the bulkiness of the POSS monomer which is expected to inhibit translation relative to the ODA, as well as aromatic interactions between the peripheries of neighboring POSS cages. The location of the POSS cage is also expected to introduce free volume into the polyimide, likely greater for the pendant moiety over the bead-on-a-string type.

The underlying physics leading to the observations presented in figures 13 and 14 are more evident in the context of these effects. For **(10a)**, the pendant configuration has a greater effect on elasticity due to its introduction of free volume and reduced propensity for CTC interactions. However, the T_g is largely unaffected due to the competing effects of inhibited chain motion and POSS-POSS interactions, especially at higher concentrations. For the copolymers containing **(8a)**, free volume introduction is likely less due to the linear configuration of the POSS segments, but the T_g may be more significantly affected due to a greater unavailability of nitrogen donor atoms located within the POSS segments. Furthermore, since the POSS cage is centered along the axis of the polymer chain, the inertia required for rotation and axial translation is expected to be significantly less than the former copolymers, thus serving to reduce the T_g a greater extent.

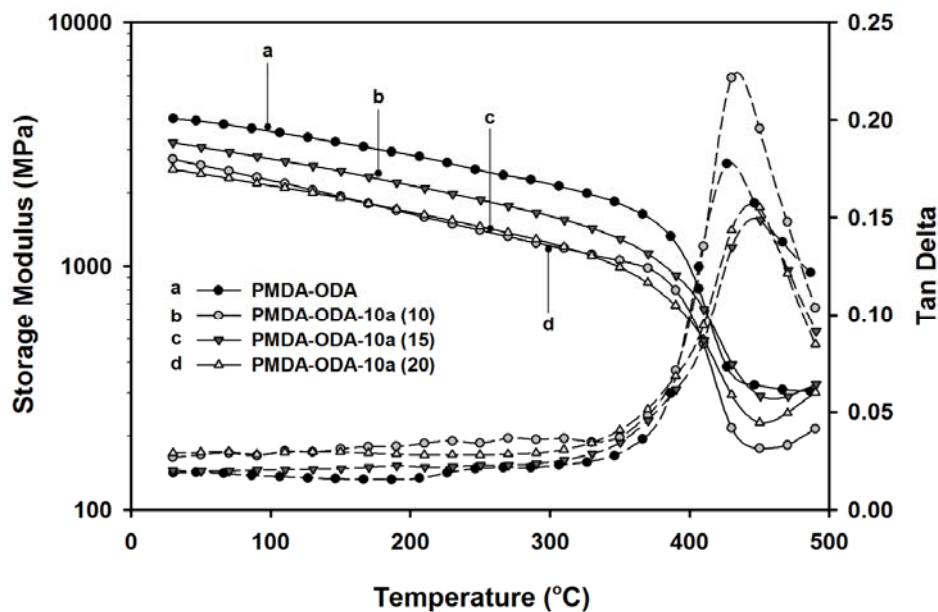


Fig. 13 Dynamic storage modulus and tan delta vs. temperature by dynamic mechanical analysis at a scan rate of 5 °C per minute for (a) PMDA-ODA and PMDA-ODA-(**10a**) copolymers, (b) 10 weight percent (**10a**), (c) 15 weight percent (**10a**), and (d) 20 weight percent (**10a**)

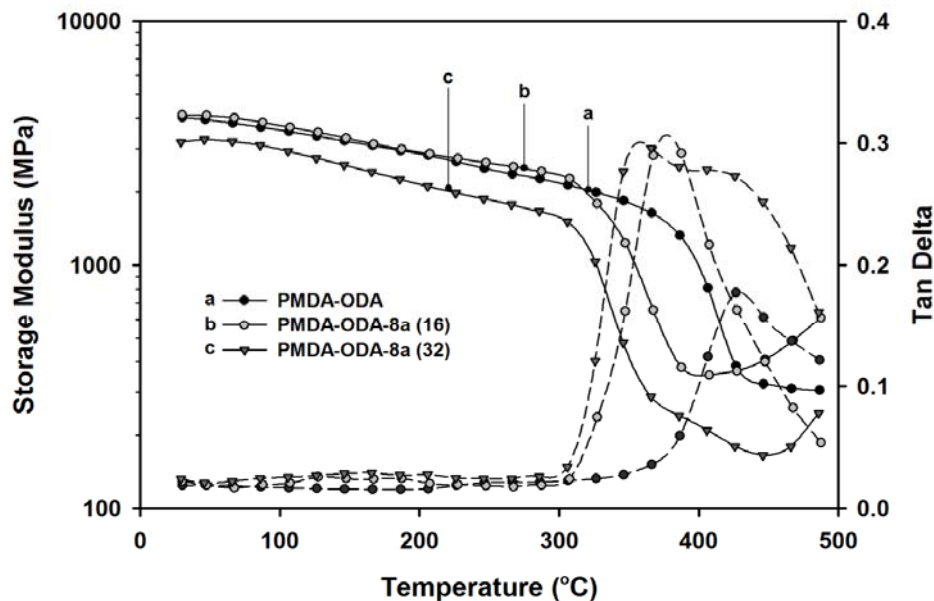


Fig. 14 Dynamic storage modulus and tan delta vs. temperature by dynamic mechanical analysis at a scan rate of 5 °C per minute for (a) PMDA-ODA and PMDA-ODA-(**8a**) copolymers, (b) 16 weight percent (**8a**), (c) 32 weight percent (**8a**)

4 Conclusions

A series of new aromatic Polyhedral Oligomeric Silsesquioxane (POSS) dianiline molecules has been synthesized for use in the preparation of high temperature aromatic polyimides. A general synthetic strategy was devised to improve the structure, yield, and utility of POSS dianilines over those currently available. Peripheral aromatic functionality was specifically incorporated in order to improve thermal properties and to increase compatibility with aromatic polymers. Silyloxy and/or aromatic functional groups were used to link the aniline

functionality to the POSS cage in order to ensure that this linkage was not a thermal weak point. Additionally, the stereochemistry of the aniline functionality has been varied to produce both meta- and para- isomers. The monomers produced have been used to produce high molecular weight polyimide polymers. These dianilines have been incorporated as pendants to the polymer backbone, as well as being incorporated into the polymer main-chain in a bead-on-a-string fashion. The nature of connectivity of the POSS cage to the polyimide backbone significantly affects delivered viscoelastic properties. In addition to producing POSS polyimides with superior thermal stability, these new monomers will allow for a full characterization and comparison of POSS-polyimides with differing structures in order to delineate the structure property relationships of POSS and polymer architectures.

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